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A Review of Recent Developments: Self-Healing Approaches for Polymeric Materials

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The development and characterization of self-healing polymeric materials are now being considered for engineering applications. This is an emerging and fascinating area of research that could significantly extend the working life and improve the safety of the polymeric components for a broad range of applications. Overviews of various self-healing approaches for polymeric materials are presented in this paper. The approaches used to achieve healing functionality can be divided into three, such as microencapsule, microvascular, and intrinsic based healing system. Microencapsulation is a process of enclosing micron-sized particles of solids, droplets of liquids, or gases in an inert shell, which in turn isolates and protects them from the external environment. Microvascular based healing system can be partitioned in a manner similar to microcapsules base healing system in terms of the design cycle. Microvascular based healing system is known to give a significant improvement and overcome a few limitations present in the microcapsule embedded self-healing membrane design. Intrinsic based healing system is inherently able to restore its integrity which requires an external trigger for the self-healing to take place. This system is less complex than the microcapsule and microvascular based healing system in achieving repair through inherent reversibility of bonding of the matrix polymer. The development of polymers that can repair damage autonomously would be useful to improve the lifetime of polymeric materials. Success in the design of self-healing materials has important consequences on the material safety, product performance and enhanced fatigue lifetime.

1. Introduction

In the last two decades, some intensive research works with self-healing abilities have been carried out. A self-healing polymer was developed that offers promise in significantly extending the life of polymeric components by autonomically healing micro cracks whenever and wherever they develop (White et al., 2001). Self-healing materials are currently in demand due to its unique and superior properties. Furthermore, self-healing materials have the ability to repair themselves and to recover their functionality using the resources inherently available to them, which offer longer-lasting products. The objective of self-healing properties is to support the system's reliability by minimising the outages. Conceptually, self-healing materials have the built-in capability to substantially recover their load transferring ability after damage.

Generally, there are various approaches that can be administered to achieve healing functionality and it can be classified into two, which are extrinsic and intrinsic based healing system. Extrinsic healing system can be divided into two groups which are microencapsulation and microvascular based healing system within the matrix which is released after cracking. Whereas the intrinsic healing system involves a reversible molecular bond in the structure of the material. Each system is distinguished by the mechanism used to sequester the healing functionality until it is triggered by damage.

Microencapsulation based healing system is processed based on the use of a healing agent contained in the matrix as a separate phase. The healing agent is usually in the liquid state, placed in the form of microcapsules

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or hollow fibres (White et al., 2001). Previously, White et al. (2001) focused on self-healing polymer composites, in which a monomer healing agent is stored in microcapsules and dispersed through an epoxy matrix. Thanawala et al. (2014) studied on the process parameters in developing microcapsules by *in-situ* polymerization of linseed oil as core and urea-formaldehyde as the shell material. Similarly, Sanada et al. (2015) also reported the healing of interfacial debonding in fibre reinforced polymers (FRPs) and it showed that the microencapsulated healing agent and solid catalyst are dispersed in the coating layer on the surface of the fibres.

Microvascular based healing system can overcome the limitations of microencapsulation based healing systems in which a finite supply of healing agents restrict the number of healing events possible. This approach has been explored and it relies on a centralized network, which is a microvascular network for distribution of healing agents into polymeric systems in a continuous pathway. Recently, Toohey et al. (2008) investigated a coating design which delivers healing agent to a crack damage in a coating via a three-dimensional microvascular network in the substrate. Similarly, Therriault et al. (2003) developed an interconnected microvascular network fabricated by direct-write assembly method. The extrinsic healing system concept is based on the response after or at the onset of damage. Furthermore, materials using extrinsic approaches are vulnerable to repeated damage at the same location. Das et al. (2016) reported the healing of structures is not possible once the healing agents are exhausted or when the containers become empty. Current research focuses on improvement of healing agents and catalysts, and on new encapsulation techniques that can react without a catalyst when released (Das et al., 2016).

In contrast, intrinsic self-healing system can recover their properties due to the presence of specific reversible chemical bonds, which is beneficial due to the possibility of multiple healing steps at the same location. These bonding can be composed of either dynamic covalent bond (such as the Diels-Alder reaction or radical-based systems) or supramolecular interactions (such as hydrogen bonding, ionomers, metal bonding, or π–π stacking). Dynamic covalent bonds are dynamic bonds within molecules through reversible formation and breaking of covalent bonds which concerns only covalent bonding interactions. Supramolecular network are intermolecular bonds which are the structure and functions of the entities formed by association of two or more chemical species. Supramolecular interactions such as hydrogen bonds or ionic interactions can reform and regenerate a network with dynamic properties by itself potentially leading to self-healing behavior. Supramolecular is an attractive method of designing small molecule systems exhibiting rubber-like elasticity.

Cracks or breaks occurring in supramolecular material can be healed by simply putting the fractured surfaces back together and applying light pressure, then the materials recover nearly all their initial strength without the need for bonding or heating. This method is mostly suitable for rubber as it requires relatively soft polymers with low glass transition temperature, Tg. After the rubber materials are damaged, the pieces may be brought back into close contact to enable reformation of the hydrogen bonds. Cordier et al. (2008) studied the self-healing and thermoreversible of rubber from supramolecular assembly, taking the approach to design and synthesize molecules that join to form both chains and crosslinks via hydrogen bonds. Montarnal et al. (2009) reported on the versatile one-pot synthesis of supramolecular plastics and self-healing rubbers, which developed a simplified synthesis for the precursor molecules for the same design strategy system. This mainly focused on grafting H-bonding onto previously synthesised appropriate backbone such as telechelic, multifunctional polymer or star shaped. The main criteria for the material to be able to display self-healing property is the presence of reactive groups such as hydroxyl, carboxylate, amine, sulphide, ketone, free radicals and cyclic structure that enable self-healing formation. Early literature suggests the use of microcapsule and microvascular based healing agents to achieve a self-healing effect, but they were unsuccessful in producing practical self-healing materials. Thus, when considering their healing repeatability and stability, supramolecular self-healing is a better approach to overcome cracks in rubber polymeric. To date, limited attention has been dedicated to developing elastomers with autonomic self-healing ability, which can recover damages without the need of an external or internal source of healing agents.

2. Approaches of self-healing

2.1 Microencapsulation based healing system

Microencapsulation is a process of enclosing micron-sized particles of solids, droplets of liquids, or gases in an inert shell. The main purpose of encapsulation is to control the release of active agent when an external condition such as mechanical stress or energy triggers the microcapsules to break, rupture or melt. The inertness is related to the reactivity of the shell to the core material. The end product of the microencapsulation process is termed as microcapsules, which has two parts, namely the core and the shell. They may have spherical or irregular shapes and may vary in size ranging from nano to micro scale. Healing agents or catalysts containing microcapsules are used to design self-healing polymer composites.

White et al. (2001) focused on self-healing polymer composites, in which a monomer healing agent is stored in microcapsules until the material is ruptured by damage and consequently dispersed through an epoxy matrix.

When the microcapsules are punctured, thedicyclopentadiene (DCPD) monomer will be dispersed within the polymer matrix where the damage occurred as shown in Figure 1. Based on Figure 1, a crack was formed in the matrix where the damage occurred (top), rupturing the microcapsules and releasing the healing agent into the crack plane through capillary action (middle), the contact between the healing agent and catalyst triggered polymerisation that bonds the crack faces closed (bottom) (White et al., 2001).
Another approach taken by Thanawala et al. (2014) reported on the development of self-healing coating based on linseed oil as an autonomous repairing agent for corrosion resistance. The development of microcapsules was by in-situ polymerisation of linseed oil as the core and urea-formaldehyde as the shell material. The effectiveness of the microcapsule in coating was characterised by analysing their performance, adhesion and mechanical properties. Sanada et al. (2005) also reported the healing of interfacial debonding in fibre reinforced polymers (FRPs) and it showed the microencapsulated healing agent and solid catalyst were dispersed in the coating layer on the surface of the fibres.

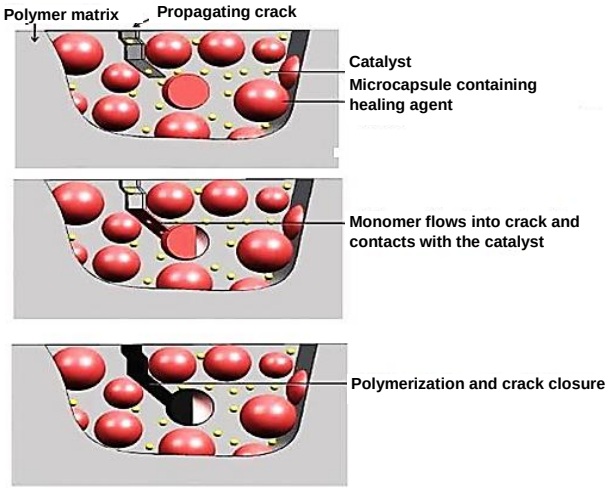

Figure 1: Schematic diagram of Microencapsulation based Healing System (White et al., 2001).

2.2 Microvascular based Healing System

The same issues from the previous healing system such as mechanical characterization trigger mechanism and performance of healing must be considered. In moving from a compartmental (microcapsule) to a circulatory (network) approach, the primary technical challenge is to design and fabricate a pervasive, interconnected, three-dimensional (3D) vascular network across multiple-length scales. While the level of vascular interconnectivity and complexity in natural systems are formidable, simplified networks have been recently fabricated and tested (Therriault et al., 2003). Preliminary results indicate that resupply of the healing agent is feasible and an extended life of the polymers can be achieved in response to repeated damage (Toohey et al., 2007).
Recently, Toohey et al. (2009) presented ways to overcome the problem of short supply of a healing agent in microcapsule based self-healing concept, which is another approach similar to biological vascular system of many plants and animals. This approach has been explored and it relied on a centralized network which is the microvascular network for distribution of healing agents into polymeric systems in a continuous pathway. In industries such as aerospace industry, damages and cracks are especially difficult to detect and observe. Another approach suggested by the experiments of Syrett et al. (2010) demonstrated that after the healing agent capsule has been used, it is impossible to add more new materials to the damaged site. However, microvascular systems have been designed to mimic the vascular system in the body. They do not provide a one-time solution for the damaged materials, instead they provide a continuous flow of healing agent to the site. This unique property makes them good candidates for future smart materials (Syrett et al., 2010).
Hansen et al. (2011) conducted the healing efficiency of the healing material and the mechanical behavior achieving healing efficiencies of approximately 70-80 % from 30–70 % healing efficiency. Through three-dimensional (3-D) microvascular network that are embedded in the substrate, the healing agent will no longer propagate to the area of cracks in the layer of materials as shown in Figure 2. Figure 2 shows the schematic diagram of microvascular based healing system where; (a) A capillary network in the dermis layer of skin with a cut in the epidermis layer; (b) The self-healing structure composed of a microvascular substrate and a brittle epoxy coating containing embedded catalyst in a four-point bending configuration monitored with an acoustic-emission sensor; (c) A high magnification cross-sectional image of the coating showing that cracks, which initiate

at the surface, propagate towards the micro channel openings at the interface (scale bar ¼ 0.5 mm); and (d) An optical image of self-healing structure after cracks are formed in the coating (with 2.5 wt% catalyst), revealing the presence of excess healing fluid on the coating surface (scale bar ¼ 5 mm) (Toohey et al., 2007).

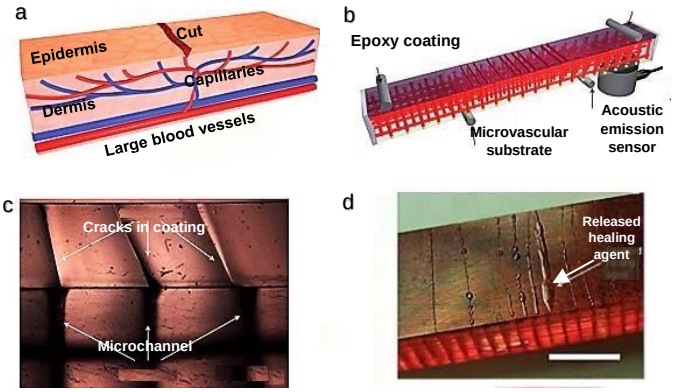

Figure 2: Schematic Diagram of Microvascular based Healing System (a) Capillary network; (b) Self-healing structure; (c) High magnification cross-sectional; (d) Optical image of self-healing structure (Toohey et al., 2007).

2.3 Intrinsic based Healing System

This system makes it less complex than the microcapsule and microvascular based healing system in achieving repair though inherent reversibility of bonding of the matrix polymer, as shown in Figure 3. For intrinsic systems, the matrix is inherently self-healing and the sequestration of healing agents is no longer required. Therefore, many of the problems with integration and healing-agent compatibility that arise in microencapsulation and microvascular based healing system can be avoided. However, intrinsic self-healing materials must meet the desired mechanical, chemical and optical properties for intended applications. Figure 3 shows the schematic diagram of intrinsic based healing system, which can be demonstrated using three main schemes. There are a few methods for achieving intrinsic healing-based system, such as intrinsic self-healing polymers based on reversible reactions, ionomeric self-healing materials, self-healing from dispersed thermoplastic polymers, self-healing via molecular diffusion and supramolecular self-healing materials.

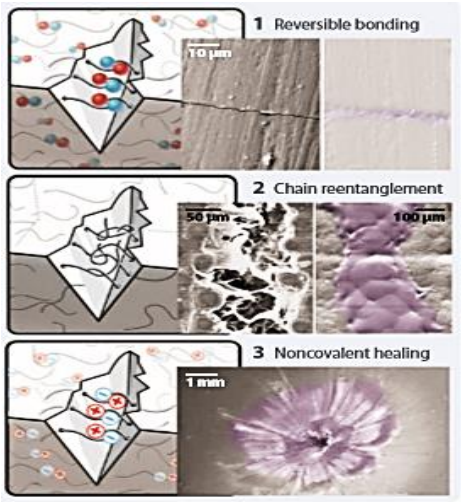

Figure 3: Schematic Diagram of Intrinsic based Healing System (Luo et al., 2009).

Firstly, self-healing materials based on reversible reactions include monomers that can be reversibly transformed from the monomeric state to the cross-linked polymeric state through the addition of external energy. The reaction scheme for remendable self-healing materials includes the retro-Diels-Alder (rDA) and Diels-Alder (DA) reactions. In particular, Chen et al. (2002) presented a study that carried out a thermally remendable crosslinked polymeric material self-healing system based on the DA reaction of synthesized furan-maleimide polymers. This process can be used to restore a fractured part of the polymer multiple times. It is fully reversible and does not require additional ingredients, for example, a catalyst, additional monomer, or a

special surface treatment of the fractured interface. Another approach taken by Park et al. (2008) demonstrated the development of a self-healing composite using a mendable polymer and resistive heating. They utilized the thermally reversible Diels–Alder reaction derived from cyclopentadiene to incorporate healing functionality and analyzed which derivative act both as the matrix and the bulk matrix in a carbon fiber composite as shows in Figure 4.

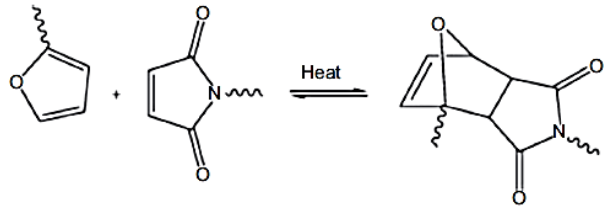

Figure 4: Mechanism of the Diels-Alder (DA) reaction for cross-linked polymers (Park et al., 2008).

Secondly, ionomeric self-healing materials which act as cross-links that can be reversed is a class of substances with ionic segments, which can form a cluster. These clusters can be activated by external stimuli such as ultraviolet (UV) irradiation and temperature. Multiple local events of healing are possible due to the formation of clusters, which is reversible. Recently, Kalista et al. (2007) demonstrated the projectile puncture testing self-healing of poly(ethylene-co-methacrylic acid) (EMAA) copolymers with ionic segments. From the experiment, the healing occurred in a two-stage process of melt elastic recovery followed by sealing and polymer chain interdiffusion at the damaged site. Polymers can be designed to form a strong end group and/or side-group associations via reversible and multiple hydrogen bonds, ionic aggregates and multiple complementary which result in a supramolecular self-healing of elastomeric polymer.

Thirdly, self-healing materials based on dispersed thermoplastics use an intrinsic, thermally activated self-healing approach. The thermoplastic polymer is selected for its good compatibility and is dissolved in the polymer matrix, resulting in a homogeneous system. After the damage, healing is triggered by a rise in temperature and pressure so that the thermoplastic healing agent can move and fill the cracks (Hayes et al., 2007). Luo et al. (2009) reported the development of thermoplastic or thermoset blend exhibiting thermal mending and reversible adhesion by dispersing phase-separated demonstrated with poly (caprolactone) (PCL) in an epoxy matrix. The recovery process of self-healing from the dispersed thermoplastic polymers occurs by the melting and subsequent re-dispersion of the thermoplastic material into the crack plane, filling the crack and mechanically interlocking with the surrounding matrix. The PCL melts and undergoes a volumetric thermal expansion to fill the damage.

Fourth, an alternate method for achieving intrinsic self-healing is self-healing via molecular diffusion. O'Connor and Wool (1980) investigated optical studies of void formation and the mechanisms involved in healing the damage in styrene-isoprene-styrene block copolymers and polystyrene. Healing was found with increase of temperature and time parameter. The phenomena of healing for these polymers were temperature and time dependent and it occurred via surface interaction, void closure, and molecular entanglement between the damaged faces. Rahmathullah and Palmese (2009) reported a crack healing behavior of epoxy-amine thermosets whereas molecular diffusion through thermal treatment of an epoxy matrix with excess amine functionality.

Lastly, Baharulrazi et al. (2017) and Salehuddin et al. (2018) carried out research on the synthesis and characterization of hydroxyl terminated epoxidized natural rubber (HTENR) via oxidative degradation and the synthesis of self-healing supramolecular HTENR demonstrated with a three-step procedure. Another approach suggested by the experiments of Cordier et al. (2008) demonstrated self-healing and thermoreversible of a rubbery material from supramolecular assembly. The process of healing can be repeated many times, and the material can be easy to process, re-used and recycled. Similarly, Montarnal et al. (2009) also developed the synthesis of supramolecular self-healing elastomers from vegetable oil fatty acid derivatives, diethylene triamine, and urea, and the preparation of oligomers with a two-step procedure. Among all methods, supramolecular is the best method due to the interaction of supramolecular, which is a promising way to develop an intrinsic healing based system. They are reversible and require low energy, they can also have a great influence on the overall mechanical properties of the material.

3. Conclusion

The approach of extrinsic based healing system (microencapsulation and microvascular) is based on the response after or at the onset of damage. Nevertheless, this concept yields materials with limited healing lifetimes since rupture of the entire microcapsule population depletes the supply of healing agent, thus healing functionality is no longer maintained. Furthermore, the materials using extrinsic approaches are vulnerable to

repeated damages at the same location and healing of structures is not possible once the healing agents are exhausted or containers become empty. However, current research focus on improving healing agents, catalysts and new encapsulation techniques that can react without a catalyst when released. Engineering materials have their own characteristic and in designing self-healing behaviors in such materials, their intrinsic or natural characteristic must be taken into account. Even though the field of self-healing materials spans for less than a decade, a surprisingly wide range of approaches have already been identified.

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